CHAPTER II
THEORETICAL BLACKGROUND

2.1 Theoretical Background

2.1.1 Chemistry of Tires

Tire is a double bond-containing polymer, which can be chemically cross-linked by vulcanization process. The main compositions of passenger tire are natural rubber, synthetic rubber, carbon black, steel, fabric, and some chemical substances.

The car tire-producing process begins with the rubber tree plantations mostly in South-East Asia. The latex is combined with carbon, oils, and sulfur. All of these-produces the black sheets of rubber. The rubber sheets are heated, and a thin string of nylon, polyester or even steel are woven into them to give rigidity. These sheets form the main basis of tire. One of the key steps in the manufacturing is called Vulcanization Process. It is a chemical process in which natural rubber consists of long hydrocarbon chains are linked to other polymer molecules by atomic bridges composed of sulfur atoms or carbon to carbon bonds. This heavily cross-linked polymer has strong covalent bonds, with strong forces between the chains. This hardens rubbers, giving much more durability, more resistance, and also the qualities of strength and elasticity.
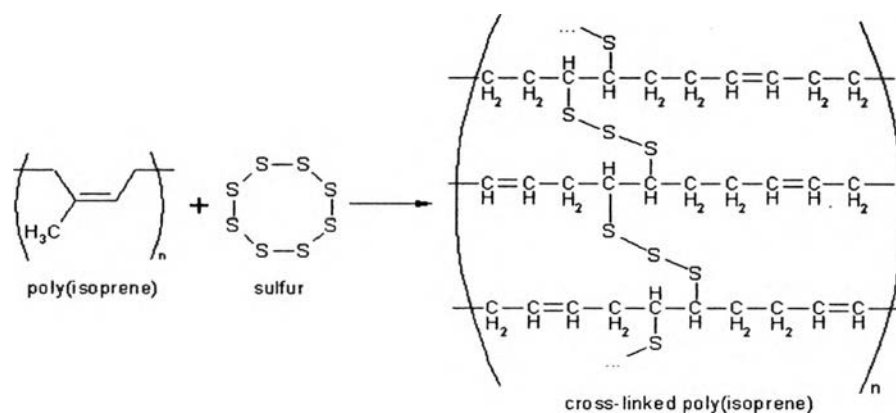

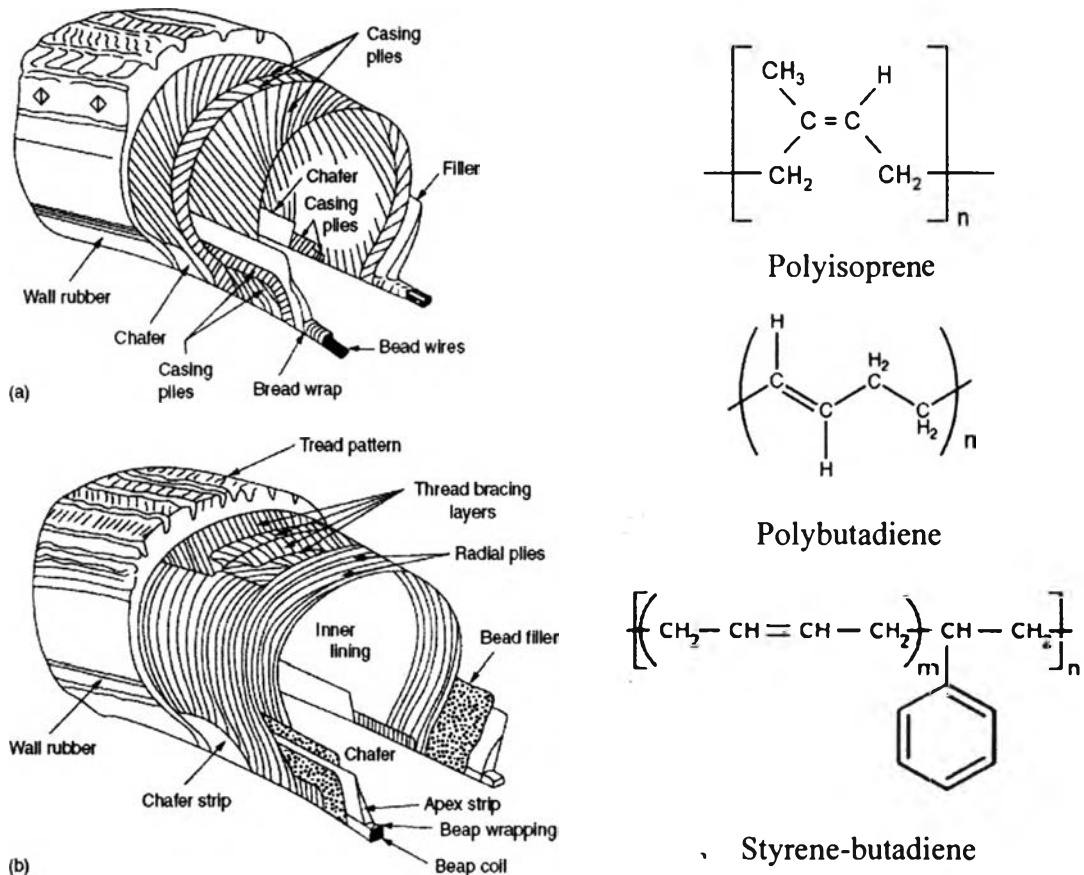
Figure 2.1 Sulfide network formation.
(http://en.wikipedia.org/wiki/File:Vulcanization.png).

Figure 2.2 Tire components and main rubber compositions in tire: (a) diagonal tire, and (b) radial tire. (http://www.aipma.net/info/plasticprocess.htm).

2.1.2 Pyrolysis of Tires

Pyrolysis is a thermal degradation process in which the material is heated indirectly in an oxygen-free atmosphere. The advantage of this process is low emission to the environment. Three products are typically obtained from the rubber: pyrolytic char, oil, and gas. Gaseous fractions are essentially composed of the high concentrations of methane, ethane, butadiene, and other hydrocarbon gases (Rodriquez *et al.*, 2001). Oil fractions consist of very complex mixtures of organic compounds or 5-20 carbons, which can be added to petroleum refinery as fuels or as a source of chemicals since they contain many aromatic and polyaromatic compounds such as benzene, toluene, xylene, and limonene. Char is a fine particulate composed of carbon black, ash, clay fillers, sulfur, zinc oxide, calcium carbonates, and silicates. It may be used as a precursor for the manufacture of low-grade

activated carbon, carbon black, and smokeless fuel. In 1999, Roy et al. found that another potentially important end-use of the pyrolytic carbon black may be as an additive for road bitumen.
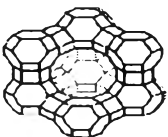
The composition of each fraction depends on:- (1) the pyrolysis conditions, (2) feed stock, (3) size of reactor, (4) type of reactor, (5) the tire composition, (6) residence time, and (7) the efficiency or heat transfer etc.

2.1.3 KL and Y Zeolites

KL zeolite, a basic catalyst, has a one-dimensional channel of 12 membered rings with a channel opening of 0.71 nm in diameter, and its nominal composition is $K_9Al_{19}Si_{27}O_{27}$ (Sato *et al.*, 1999). KL zeolite could act like an electron donor and increase the electron density on the metal clusters. The formation of "electron-rich" was proposed on the basis of IR, EXAFS, and catalyst data (Stakheev and Shpiro, 1995). Moreover, KL zeolite is often used as a supporter for highly dispersed Pt. The Pt/KL was reported as a very selective catalyst for the aromatization of n-hexane to benzene. The high aromatization activity of the catalyst was ascribed to both geometric and electronic effects.

Another type of catalyst is Y zeolite, an acid catalyst, which has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes. The pore diameter is as large as 7.4Å since the aperture is defined by a 12 membered oxygen ring, and leads into a larger cavity of diameter 12 Å. The cavity is surrounded by ten sodalite cages connected on their hexagonal faces (also known as double 6-rings). This structure can be viewed as the diamond structure, with the sodalite cages playing the role of carbon atoms, and the double 6-rings the role of C-C bonds (www.personal.utulsa.edu).

Table 2.1 The structure of KL and Y zeolites (www.chemistry.nus.edu.sg)

Zeolite		Dimension	Si/Al	Pore size (Å)
KL		1 D	6	7.1
Y		3 D	2.43	7.4

2.2 Literature Review

2.2.1 The Influence of Operating Conditions

Many researchers have studied the pyrolysis of used tires without catalysts. The influence of temperature was studied by Rodriquez *et al.* (2001) on the pyrolysis of scraps tires under nitrogen in an autoclave reactor at different temperatures. They found that the temperature of above 500°C had no significant influence on the amounts and characteristics of pyrolysis products. Thus, they concluded that 500°C was the optimum temperature for tire pyrolysis since the constituent rubbers were completely decomposed. Likewise, Roy *et al.* (1999) studied tire pyrolysis in the temperature range of 350 to 700°C. They found that pyrolysis temperature did not affect the yields over 500°C. Similarly in 2006, Murillo *et al.* studied the influence of heating rate, flow rate, particle size, and temperature on waste tire pyrolysis. They also found that at the temperatures below 500°C, the conversion depended on temperature, and at the temperature higher than 500°C, the reaction was complete because the conversion was not improved. Moreover, there was the influence of the reaction time in the range of 15-60 min and

the heating rate in the range of 25 to 300°C/min on the total conversion and oil yield. And in 2004, Laresgoiti *et al.* studied the pyrolysis of a whole car tire under nitrogen atmosphere in an autoclave at temperatures between 300 to 700°C. They showed that temperature affected to the yields of liquid and gas obtained from the process. And, the concentration of aromatic hydrocarbon increased with the temperatures up to 500°C. William *et al.* (1990) studied the pyrolysis of scrap automotive tire under nitrogen atmosphere in a static-bed reactor. They found that gas and oil yield increased until the pyrolysis temperature reached 600°C, and they concluded that the increase in pyrolysis temperature affected to the amount of hydrocarbon in oil fraction. The aliphatic hydrocarbons were decreased whereas aromatic hydrocarbons were increased.

In 2002, Galvagno *et al.* varied the process temperatures between 550 to 680°C. They found that the higher temperatures promoted the secondary reactions of the volatile fraction. They showed that carbon content in gas phase grew with temperature. Moreover, the calorific value of gaseous fraction also increased with temperature. Berrueco *et al.* (2005) studied tire pyrolysis in an atmospheric static-bed reactor under nitrogen atmosphere in the temperature range of 400 to 700°C. They found that the liquid yield was increased at the temperatures of 400 to 500°C and remained constant until 700°C, whereas the gas yield slightly increased at the temperature range of 400 to 700°C. They concluded that the yield of light gas increased at high pyrolysis temperatures. In the contrary, Cunliffe and William (1998) studied waste scarp tire pyrolysis in a static-bed reactor at the temperature range 450 to 600°C. They discovered that the liquid fraction decreased while the gaseous fraction increased when increasing the final pyrolysis temperature of the reactor. The same results were obtained by Lee *et al.* (1995), who studied the effect of the feed rate of waste tire at the pyrolysis temperature range 700 to 880°C. They found that the gas product increased while the liquid product decreased with the increasing temperature. They concluded that the compositions, heating value, and product yields were independent of the feed rate of waste tire. Likewise, Leung *et al.* (2002) studied the pyrolysis of tire powder between 500 to 1000 °C. They discovered that gas yield increased with increasing temperature because of thermal cracking, and also increased with residence time at temperature above 700 °C, but lower heating

value (LHV) was decreased. Furthermore, they noted that about 57% sulfur was retained in char and 6% in gas phase. Mastral *et al.* (2000) studied scrap tire pyrolysis from 400 to 600 °C. They found that total conversion and oil yield decreased at the temperatures below 500 °C, and remained constant at the temperatures above 600 °C. Diez *et al.* (2004) studied the influence of final temperature on the calorific valve of products. They found that the liquid fraction from tire pyrolysis had a high calorific value of up to 40 MJ/kg, which increased along the increasing temperature. Decreasing of CO_2 and increasing of CO from the secondary reactions taking place during the process were also observed at higher temperatures.

2.2.2 Catalytic Pyrolysis

This technique is another way to improve either the quality or quantity of pyrolysis products. The catalyst plays an important role on modifying the product yields and the compositions of hydrocarbon products. Moreover, this technique can reduce the processing time and the temperature to decompose the tire rubbers. Several researchers studied the effect of zeolite in pyrolysis of waste tires. Shen *et al.* (2006) studied the pyrolysis of scrap tires by using USY zeolite catalyst. They investigated the influence of pyrolysis temperature, catalytic temperature, catalyst/tire ratio, and heating rate. They reported that when the temperature and catalyst/tire ratio were increased, the high gas yield and coke formation were observed. Li *et al.* (2005) studied the influence factor on catalytic pyrolysis process. They found that the keys to get high productivity were the properties of feedstock and the types of catalyst. They also concluded that for different cracking feedstock, the yield of light olefins increased over the same types of catalyst. Similarly, Vitolo *et al.* (1999) reported that the obtained products depended on the characteristics of catalyst. The aromatic hydrocarbon products were obtained when a strong acid and shape selective HZSM-5 zeolite was used, whereas mostly aliphatic hydrocarbons were produced when silica-alumina was used. And they also found that the upgraded liquid obtained by using the HZSM-5 might be easily separated from the aqueous phase while the liquid obtained by using the HY zeolite were either dispersed or dissolved in the water.

In 2007, Marcilla *et al.* studied the catalytic pyrolysis of LDPE over H-Beta and HZSM-5 zeolites in dynamic conditions. They found that Beta zeolite gave higher selectivity to C_4 and C_5 compounds at the different temperatures. Beta zeolite also has the ability in cracking naphthenes or aromatic-naphthanic rings. In 2001, Corma *et al.* studied Beta zeolite on cracking tetraline and decaline. The results showed that the large pore size of Beta zeolite was suitable for cracking naphthenes and fused aromatic-naphthanic rings in a light cycle oil, and better suited for hydrotreating a light cycle oil. And they also studied the catalytic cracking of n-heptane on MCM-22 and compared with ZSM-5 and Beta zeolites. They found that Beta zeolite gave the high ratios of alkane/alkene and iso-butane/total butane. Likewise, Bonetto *et al.*, (1992) reported that Beta zeolite produced relatively high iso-butane yield in gas oil cracking process. Miguel *et al.* (2006) investigated the effect of five acid catalysts in the conversion of tire rubber into hydrocarbon products. They found that all zeolite catalysts gave a marked selectivity of aromatics species, especially toluene, m/p-xylene and benzene. And, they also found that Beta zeolite produced high single aromatic content in oil product, but provided lower aromatic capacity due to weaker acid site as compared with the other zeolites. Similarly, William *et al.* (2003) studied the effect of ZSM-5 and Y Zeolites with different pore sizes and Si/Al ratios. The result showed that the oil products had high single ring aromatic compounds such as toluene, benzene, and xylene when the Y zeolite with low Si/Al ratio was used. They also found that lower pore size zeolite (ZSM-5) produced lower aromatic compounds as compared with large pore size zeolite (Y zeolite).

2.2.3 Supported Platinum Catalysts

One of the most interesting series of catalysts used in catalytic pyrolysis is bifunctional catalysts because they can reduce polyaromatic hydrocarbons in the oil due to their high activity and selectivity for the hydrogenation and ring opening of aromatic hydrocarbon. In 1997, Corma *et al.* studied a Pt/MCM-41 catalyst on the hydrogenation of aromatics in diesel fuel. The results showed that the Pt/MCM-41 had the superior hydrogenation activity of naphthalene feed than other conventional Pt-containing supports. They also found

that Pt/MCM-41 was a very stable catalyst towards poisoning by sulfur. Likewise, Song (2000) reported that the Mordenite-supported Pd catalyst was more active and more sulfur-resistant than the same metal on Y zeolite at the same metal loading level. Platinum supported on the same Mordenite had less sulfur resistance than Pd supported catalyst. They concluded that the structure of zeolite and the type of metal were important for the sulfur tolerance. Roldán et al. (2005) studied the influence of acidity and pore geometry on the product distribution in the hydroisomerization of light paraffins in order to improve octane number of gasoline. They found that Pt/USY, Pt/Mordernite, and Pt/Beta gave a high selectivity of isomerized products of light naphtha. In 2002, Arribas and Martinez tried to upgrade the diesel quality on coupling hydrogenation and the ring opening of 1-methylnaphthalene by using a Pt/USY catalyst. They reported that the major components of ring opening products (ROP) with high cetane numbers were C_{11}alkylbenzene, C_{11}cyclohexane, and C_{11}cyclopentane. And in 2004, Arribas et al. investigated the influence of the metal function of Pt/USY catalysts in the combined hydrogenation and the ring opening of tertralin. They found that the rate of isomerization and ring opening increased with increasing the Pt loading in the range of 0.25-0.4 %wt, indicating that the rate-determining step was the dehydrogenation of the naphthene on the metal sites.

There have been a few researches that studied the effect of the activity of platinum supported on Y zeolite catalyst since the acidity of the catalyst has a major effect on the hydroisomerization and hydrocracking. In 2004, Santikunaporn et al. studied the ring opening of decalin and tetralin on HY and Pt/HY zelolite catalysts result in an improvement in cetane number. They investigated that the production of ring opening products was greatly enhanced in the presence of platinum. Cheon Park and Ki Ihm (2000) investigated the effect of bifunctional platinum catalysts containing ZSM-5, ZSM-22, SAPO-11, Al-MCM-41, H-Y and H-β on the hydroisomerization of n-hexadecane under reaction condition of 350 °C and 103 bar. They reported that Pt/ZSM-5, Pt/ZSM-22 and Pt/H-β catalysts with strong acid sites showed higher hydrocracking activity whereas Pt/SAPO-11, Pt/Al-MCM-41 and Pt/H-Y catalysts showed better isomerization selectivity due to their moderate acid strength. And in 2002, William and Brindle studied the influence of the temperature in the catalytic prolysis using two zeolites with different pore

sizes, Y-type zeolite and ZSM-5. They found that Y-type zeolite which has larger pore size and higher surface acidity and also Y-type zeolite yielded higher aromatic compounds but lower liquid yields than ZSM-5 catalyst.

Furthermore, KL Zeolite has the good properties, but there have been a few researches that used this zeolite in the catalytic prolysis of tire. In 1999, Bécue *et al.* investigated the behavior of the different alkali catalysts on the aromatization selectivity. They found that Pt/KL has the highest aromatization selectivity. Therefore, the octane number of gasoline should be increased by using Pt/KL. Barrer and Villiger (1969) found that the platinum catalyst supported by KL zeolite had a highly selective catalyst for aromatization of n-hexane. Álvarez-Rodríquez *et al.* (2005) also found that the ruthenium supported on KL zeolites showed selectivities and activities on hydrogenation of unsaturated aldehyde. Kumar *et al.* (2008) studied the effect of preparation variables on the aromatization activity of Pt/KL catalysts. The light naphtha containing C5, C6 paraffin and naphthenes was used as a feed for the activity studies. They reported that the BKL-0.4 catalyst prepared with 0.4 wt% of Pt loaded on the basic 'binder containing KL support exhibited better catalytic properties such as no loss in pore volume and surface area after metal loading. They also found that above 0.4 wt% Pt loadings, the catalyst exhibited a decrease in the pore volume, and the dispersion of Pt indicated the Pt agglomeration at above 0.4 wt% loading in the zeolite pores. Moreover, the studies indicated the incipient wetness impregnation method can be used for the preparation of active and stable catalysts for aromatization by following the principle of optimum metal loading, where pore volume analysis can provide valuable information. Jacobs *et al.* (2001) also indicated that the Pt loading by vapor phase impregnation method is efficient on powdered KL but not on the extrudates. That means the efficiency of the vapor phase impregnation is decreased in the presence of the binder material in the extrudates.

The n-octane aromatization studied by Jongpatiwut *et al.* (2003) suggested the diffusion constraints on xylenes in the sample prepared by VPI method when the amount of Pt was 1.0 wt%. Similarly, Trakarnroek *et al.* (2006) investigated the effect of various morphologies and channel lengths of the KL zeolite on the n-octane aromatization reaction. The results showed that zeolites with longer

channels and irregular pore month structure prolong the residence time of C8-aromatics, and increased the concentration of benzene and toluene in the products. They also found that the catalysts with very small crystal size were preferred for producing higher C8-aromatics. Moreover, the high selectivity to C8-aromatics can be obtained form the Pt/KL zeolite having more Pt located near the pore mouth.

2.2.4 Mixed Catalysts

As is well known, the preparation of catalysts with enhanced properties could be achieved in many ways, such as by using a new support, new active species and new promoters. A few researches have focused on mixed catalysts to increase yield and reduce deactivation for cracking and hydroprocessing catalysts. For example, Fan el at. (2005) studied a novel catalyst having excellent olefin reduction without a loss in the octane number of gasoline. The result showed that the series of HMOR/Beta/ZSM-5/SAPO-11 zeolites gave a high liquid yield, improved gasoline RON because of high iso-paraffins (C5-C6) arenes (C8-C10), and lowered the amount of coke deposit on the catalysts. They' also reported that HMOR/H-Beta/SAPO-11 were good catalysts for hydroisomerization while HZSM-5 was good for aromatization. Furthermore, they investigated that the stronger acidity favored aromatization at high temperatures, but lowered stability because of coke formation. Serra et al. (2005) designed a multizeolitic catalyst to optimize the dealkylation of ethyl and propyl aromatics in order to maximize xylene yield during the processing of heavy reformate. They found than a catalyst formulation (ZSM-5 40%, Beta 60%, and Re 0.26%) gave maximize the yield of xylene (34%).
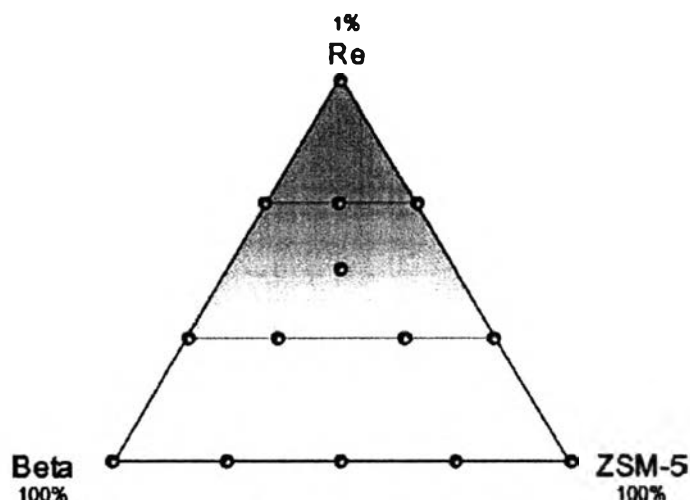
Figure 2.3 Mixture design for the system of ZSM-5/beta/rhenium. (Serra *et al.*, 2005).

And in 1999, Oloruunyolemi and Kydd studied the cracking, hydrocracking, and hydrodesulfurization activities of gallium-aluminium mixed oxide catalysts, with fluoride added as a promoter. The result showed that the addition of fluoride to the Ni-Mo catalyst supported on the mixed oxides enhanced the cracking and the hydrocracking reactions of the catalysts. And, they also found that the presence of gallium could reduce coke formation. In 1998, Byggningsbacka *et al.* investigated the formation of isobutene from n-butane over a zinc-impregnated potassium-ion-exchanged ZSM-5 dehydrogenation catalyst and and acidic shape-selective ZSM-22 skeletal isomerization catalyst. The results indicated that the zinc-impregnated ZSM-5 gave a high selectivity of dehydrogenation catalyst for transforming n-butane to n-butene because the zinc-impregnated ZSM-5 providing Brønsted acidity was reduced by potassium ion exchange before zinc impregnation. They also found that the yield of isobutene increased after adding the acidic ZSM-22 skeletal isomerization catalyst.

In 2006, Ou *et al.* illustrated the performance for ethylene and propylene production from a catalyst consisting of a metal-based component and a solid acid component. For the first example, three catalysts were tested. The first one was a 1 g of V/Mg (V_2O_5 50%wt) oxide component. The second one was a 1.0 g

sample of steamed OlefinMax. The third one was a mixture of 1 g of V/Mg oxide and 1.0 g of OlefinMax. The results showed that yields of ethylene and propylene from the combined catalyst were higher than the combined yields of each individual component. For the next example, they used the SAPO-type solid acid components for combined oxydehydrogenation/acid cracking. In each case, 1 g of V/Mg (V_2O_5 50%wt) oxide component was mixed with either OlefinsMAX, SAPO-34, or SAPO-11. They reported that a synergistic effect was still evident between the SAPO structures and the metal-based component as a result of the low butadiene yields. And also the SAPO structure gave the lower yields of the less desirable ethane and propane as well as lower aromatic yields. For the last example, they illustrated the benefit of catalyst with an n-hexane feed. Three catalysts were tested: 1 g of V/Mg (V_2O_5 50%wt) oxide component, a mixture of 1 g of V/Mg (V_2O_5 50%wt) oxide and 1 g of SAPO-34. The results showed that V/Mg (V_2O_5 50%wt) oxide alone gave a large yield of the undesirable benzene product whereas the solid acid alone produced a low conversion and low yields of ethylene and propylene products. The mixed catalyst gave a high conversion of ethylene, propylene, and butylenes that are higher than the sum of yields of the individual components. And also a lower yield of benzene was obtained. They concluded that the formation of benzene was interrupted by the formation of the desired light olefins.

In addition, the two process options for converting aromatics into a high-quality synthetic steamcracker feed have been discovered (Weitkamp *et al.*, 2001). In 2001, Weitkamp *et al.* studied a direct route using bifunctional zeolite catalysts and a two-stage route comprising ring hydrogenation on conventional catalysts followed by the ring opening of the resulting cycloalkane on acid zeolite catalysts in the conversion of pyrolysis gasoline from naphtha steamcracker into ethane, propane, and n-butane, refered to as C_{2+}-n-alkanes. They found that in the two-stage route, the yield of C_{2+}-n-alkanes from either BTX aromatics or their cycloalkane derivatives were as high as 70% to over 90%. And the yield of undesired methane can be kept very low (typically 3-4%).
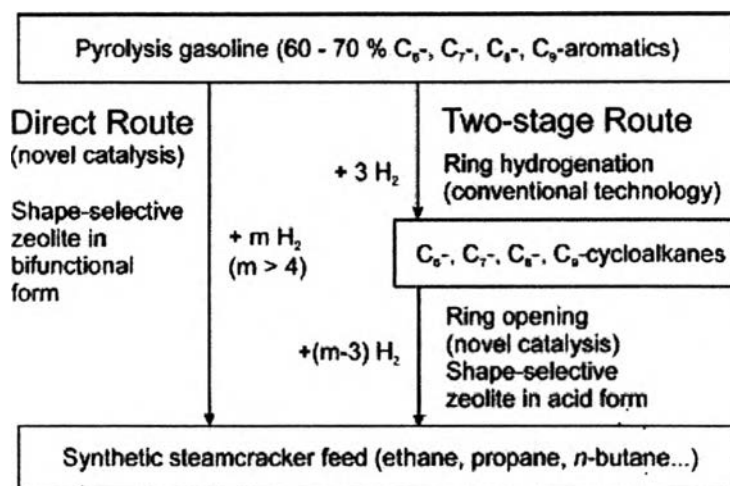
Pyrolysis gasoline (60 - 70 % C_6-, C_7-, C_8-, C_9-aromatics)

Direct Route
(novel catalysis)

Shape-selective
zeolite in
bifunctional
form

+ 3 H_2

+ m H_2
(m > 4)

+(m-3) H_2

Two-stage Route
Ring hydrogenation
(conventional technology)

C_6-. C_7-. C_8-. C_9-cycloalkanes

Ring opening
(novel catalysis)
Shape-selective
zeolite in acid form

Synthetic steamcracker feed (ethane, propane, n-butane...)

Figure 2.4 Direct and two-stage routes for converting pyrolysis gasoline into C_2+-n-alkanes, a high-quality synthetic feedstock for steamcrackers. (Weitkamp *al et.,* 2001).

As we known that, the isomerization, the aromatization, and the ring opening reaction have been performed to boot the octane number of gasoline from the heavy pyrolytic product. Thus, platinum supported on binary-catalyst systems will be investigated to enhance molecules of higher octane numbers. The potential characteristics of each zeolite are the followings: (1) platinum loading enhancing the hydrogenation and hydrocracking of large aromatic molecules, (2) Pt/KL which has the high aromatization selectivity. Therefore, the octane number of gasoline could be increased by using Pt/KL, and (3) Pt/Y zeolite catalyst which has a major effect on the hydroisomerization, hydrocracking, and ring opening reaction. It is proposed that the distribution of monobranched and multibraned isomer products can be observed.